

CLAIMS

What is claimed is:

1. A fluorine-containing copolymer comprising ;
  - (a.) a first repeat unit derived from an ethylenically unsaturated compound containing a functional group having the structure:

-X<sub>r</sub>(CH<sub>2</sub>)<sub>q</sub>C(R<sub>f</sub>)(R<sub>f'</sub>)OH

wherein  
R<sub>f</sub> and R<sub>f'</sub> are the same or different C<sub>1</sub>-C<sub>10</sub> fluoroalkyl groups, or taken together are (CF<sub>2</sub>)<sub>n</sub>;  
n is an integer from 2 to 10;  
X is S, O, N, or P;  
q = 0 and r = 0, or q = 1 and r = 0 or 1; and
  - (b.) a second repeat unit derived from an acrylate selected from the group consisting of CH<sub>2</sub>=CRCO<sub>2</sub>R" and CH<sub>2</sub>=C(CH<sub>2</sub>OH)CO<sub>2</sub>R'',  
wherein  
R is H, F, or a C<sub>1</sub>-C<sub>5</sub> alkyl or fluoroalkyl group;  
R" is a polycyclic C<sub>5</sub>-C<sub>50</sub> alkyl group containing at least one hydroxy group; and  
R''' is a C<sub>1</sub>-C<sub>25</sub> alkyl group.
2. The fluorine-containing copolymer of Claim 1, wherein (b) is tert-butyl hydroxymethylacrylate.
3. The fluorine-containing copolymer of Claim 1, wherein (b) is hydroxyadamantyl acrylate.
4. The fluorine-containing copolymer of Claim 3, wherein the polymer further comprises a repeat unit derived from 2-methyl-2-adamantyl acrylate.
5. The fluorine-containing copolymer of Claim 4 made by a semi-batch synthesis.
6. The fluorine-containing copolymer of Claim 1, further comprising a repeat unit derived from a fluoroolefin selected from the group of ethylenically unsaturated compounds containing at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom.
7. The fluorine-containing copolymer of Claim 6, wherein the fluoroolefin is selected from the group consisting of tetrafluoroethylene,

chlorotrifluoroethylene, hexafluoropropylene, trifluoroethylene, and R<sub>f</sub>OCF=CF<sub>2</sub> wherein R<sub>f</sub> is a saturated fluoroalkyl group of from 1 to 10 carbon atoms.

8. The fluorine-containing copolymer of Claim 1, wherein r=0 and q=0.
- 5 9. The fluorine-containing copolymer of Claim 1, wherein q=1 and r=0.
- 10 10. The fluorine-containing copolymer of Claim 1, wherein q=1 and r=1 and X is S, O, N or P.
11. The fluorine-containing copolymer of Claim 1, further comprising a repeat unit derived from at least one ethylenically unsaturated compound containing a functional group having the structure



15 wherein R<sub>f</sub> and R'<sub>f</sub> are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms or taken together are (CF<sub>2</sub>)<sub>n</sub> wherein n is 2 to 10 and R<sub>a</sub> is an acid- or base-labile protecting group.

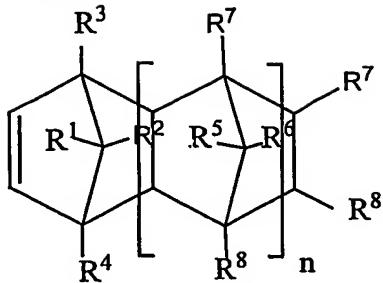
12. The fluorine-containing copolymer of Claim 11, wherein R<sub>a</sub> is CH<sub>2</sub>OCH<sub>2</sub>R<sub>15</sub>, and R<sub>15</sub> is hydrogen, a linear C<sub>1</sub>-C<sub>10</sub> alkyl, or a branched C<sub>3</sub>-C<sub>10</sub> alkyl group.

20 13. The fluorine-containing copolymer of Claim 1, wherein the functional group of repeat unit (a) is -C(CF<sub>3</sub>)<sub>2</sub>OH.

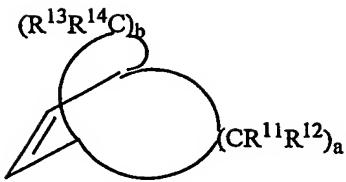
14. The fluorine-containing copolymer of Claim 6, wherein at least 25 one repeat unit is cyclic or polycyclic.

15. The fluorine-containing copolymer of Claim 6, further comprising a repeat unit derived from a cyclic or polycyclic unsaturated compound, selected from the group of compounds represented by structures (H) or (I),

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(H)



(I)

**wherein:**

n is 0, 1 or 2;

a and b are independently 1, 2 or 3, except that a is not 1 when

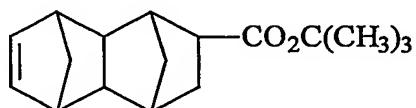
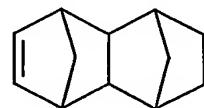
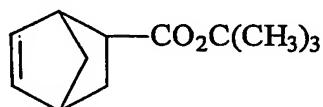
5 b is 2 or vice versa; and

R<sup>1</sup> to R<sup>8</sup> and R<sup>11</sup> to R<sup>14</sup> are the same or different, and each represents a hydrogen atom, a halogen atom, a carboxyl group, a C<sub>3</sub> to C<sub>14</sub> secondary or tertiary alkyl carboxylate, a hydrocarbon group or a substituted hydrocarbon group.

10 16. The fluorine-containing copolymer of Claim 15, wherein the cyclic or polycyclic unsaturated compound is selected from the group consisting of:

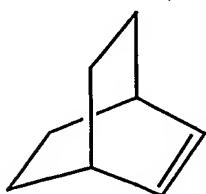


(norbornene),

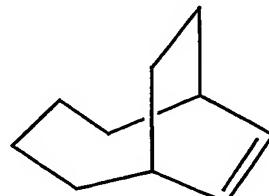


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16. The fluorine-containing copolymer of Claim 15, wherein the cyclic or polycyclic unsaturated compound is selected from the group consisting of:



(bicyclo[2.2.2]oct-2-ene),



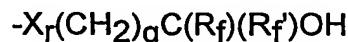
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18. The fluorine-containing copolymer of Claim 7, wherein the fluoroolefin is tetrafluoroethylene.

19. A photoresist comprising:

(a) a fluorine-containing copolymer comprising:

5 (i) a first repeat unit derived from an ethylenically unsaturated compound containing a functional group having the structure:



10 wherein

R<sub>f</sub> and R<sub>f'</sub> are the same or different C<sub>1</sub>-C<sub>10</sub> fluoroalkyl groups, or taken together are (CF<sub>2</sub>)<sub>n</sub>;

n is an integer from 2 to 10;

X is S, O, N, or P;

15 q = 0 and r = 0, or q = 1 and r = 0 or 1; and

(ii) a second repeat unit derived from an acrylate selected from the group consisting of CH<sub>2</sub>=CRCO<sub>2</sub>R" and CH<sub>2</sub>=C(CH<sub>2</sub>OH)CO<sub>2</sub>R",

wherein

20 R is H, F, or a C<sub>1</sub>-C<sub>5</sub> alkyl or fluoroalkyl group;

R" is a polycyclic C<sub>5</sub>-C<sub>50</sub> alkyl group containing at least one hydroxy group; and

R''' is a C<sub>1</sub>-C<sub>25</sub> alkyl group; and

(b) at least one photoactive component.

25 20. The photoresist of Claim 19, further comprising a dissolution inhibitor.

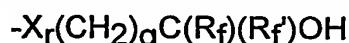
21. The photoresist of Claim 19, further comprising a solvent.

22. A process for preparing a photoresist image on a substrate comprising, in order:

30 (1) applying a coatable photoresist composition on a substrate, wherein the coatable photoresist composition comprises:

(a) a fluorine-containing copolymer comprising:

(i) a first repeat unit derived from an ethylenically unsaturated compound containing a functional group having the structure:



35 wherein

R<sub>f</sub> and R'<sub>f</sub> are the same or different C<sub>1</sub>-C<sub>10</sub> fluoroalkyl groups, or taken together are (CF<sub>2</sub>)<sub>n</sub>;

n is an integer from 2 to 10;

X is S, O, N, or P;

5 q = 0 and r = 0, or q = 1 and r = 0 or 1; and

(ii) a second repeat unit derived from an acrylate selected from the group consisting of CH<sub>2</sub>=CRCO<sub>2</sub>R" and CH<sub>2</sub>=C(CH<sub>2</sub>OH)CO<sub>2</sub>R",

wherein

10 R is H, F, or a C<sub>1</sub>-C<sub>5</sub> alkyl or fluoroalkyl group;

R" is a polycyclic C<sub>5</sub>-C<sub>50</sub> alkyl group containing at least one hydroxy group; and

R''' is a C<sub>1</sub>-C<sub>25</sub> alkyl group; and

(b) a photoactive component;

15 (c) a solvent; and

(2) drying the coatable photoresist composition to substantially remove the solvent to form a photoresist layer on the substrate;

(3) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

20 (4) developing the exposed photoresist layer having imaged and non-imaged areas to form a relief image on the substrate.

23. The process of Claim 22, wherein R<sub>f</sub> and R'<sub>f</sub> of the fluorine-containing copolymer are CF<sub>3</sub>.

24. The process of Claim 22, wherein the developing step is performed with an aqueous alkaline developer.

25. The process of Claim 22, wherein the developing step is performed with a developer selected from the group consisting of a critical fluid, a halogenated organic solvent, and a non-halogenated organic solvent.

26. The process of Claim 25, wherein the critical fluid is carbon dioxide.

27. The process of Claim 25, wherein the halogenated solvent is a fluorocarbon compound.

28. An article of manufacture comprising a substrate coated with a photoresist composition of Claim 19.